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This amendment to the Best Demonstrated and Available Technology (BDAT) Background Document for F001-F005 Spent Solvents presents the new data received by EPA and provides EPA's rationale for revising the treatment standard for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry. Section 1.0 provides EPA's legal authority for revision of the treatment standard. Sections 2.0 through 4.0 describe the specific revisions to the November 7, 1986 BDAT Background Document for F001-F005 Spent Solvents.

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AMENDMENT TO THE

BEST DEMONSTRATED AVAILABLE TECHNOLOGY (BDAT) BACKGROUND DOCUMENT FOR F001-F005 SPENT SOLVENTS - VOLUMES 1 AND 2

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EXECUTIVE SUMMARY

On November 7, 1986, pursuant to the Hazardous and Solid Waste Amendments (HSWA) enacted on November 8, 1984, the Environmental Protection Agency (EPA) established best demonstrated available technology (BDAT) treatment standards for the land disposal of EPA listed hazardous wastes identified in 40 CFR 261.31 as F001-F005. These standards apply to wastewaters and nonwastewaters for 25 spent solvents, including methylene chloride. Compliance with these BDAT treatment standards is a prerequisite for placement of the wastes in units designated as land disposal units according to 40 CFR Part 268.

EPA established a separate F001-F005 treatment standard for methylene chloride in wastewaters from the pharmaceuticals manufacturing industry. EPA has acquired additional data and is revising the treatment standard. The treatment standard promulgated on November 7, 1986 is 12.7 ppm; the revised treatment standard is 0.44 ppm. All other treatment standards promulgated on November 7, 1986, are not being revised, and therefore, remain unchanged.

This amendment to the Best Demonstrated and Available Technology (BDAT) Background Document for F001-F005 Spent Solvents presents the new data received by EPA and provides EPA's rationale for revising the treatment standard for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry. Section 1.0 provides EPA's legal authority for

revision of the treatment standard. Sections 2.0 through 4.0 describe the specific revisions to the November 7, 1986 BDAT Background Document for F001-F005 Spent Solvents.

1.0 AMENDMENT TO SECTION 1.0 OF THE BDAT BACKGROUND DOCUMENT FOR F001-F005 SPENT SOLVENTS

This section of the amendment supplements Section 1.1, Legal Background, of the BDAT Background Document for F001-F005 Spent Solvents.

On November 7, 1986 (51 Federal Register 40572), EPA promulgated treatment standards for regulated constituents in F001-F005 spent solvent wastewaters and nonwastewaters, including methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry. Since November 7, 1986, new data have become available to the Agency on the steam stripping of methylene chloride in wastewaters determined to be more difficult to treat than the F001-F005 wastewaters from the pharmaceuticals manufacturing industry. RCRA Section 3004(m) states that the Agency has the right to revise a treatment standard provided that rulemaking procedures are followed; therefore, based on the new data, EPA is revising the treatment standard for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry.

On January 14, 1986, the Agency proposed treatment standards for regulated constituents in F001-F005 wastewaters and nonwastewaters. In that proposed rule, EPA established BDAT treatment standards based on health-based standards, and the Agency determined that both biological treatment and steam stripping could achieve BDAT levels of performance for methylene chloride in F001-F005 wastewaters. F001-F005 wastewaters from the pharmaceuticals

manufacturing industry were not determined to be a separate waste treatability group in the proposed rule.

After the January 14, 1986 proposal, EPA received comments from industry (Reference 1), presenting data from plant A on the steam stripping of methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry. These data indicate that F001-F005 wastewaters from the pharmaceuticals manufacturing industry warrant a separate waste treatability group due to high concentrations of methylene chloride in the wastewaters as compared to the levels of methylene chloride in other F001-F005 wastewaters. Therefore, on September 5, 1986, EPA published a Notice of Data Availability presenting the data from plant A and asking for data and comments concerning the proposed rule.

During the comment period for the Notice of Data Availability, the Agency did not receive any additional treatment data for wastewaters from the pharmaceuticals manufacturing industry. Therefore, on November 7, 1986, EPA promulgated treatment standards for regulated constituents in F001-F005 wastewaters and nonwastewaters, including a treatment standard of 12.7 ppm for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry. The value of 12.7 ppm was based on the data for steam stripping of methylene chloride in F001-F005 wastewaters from plant A. Documentation for the calculation of this treatment standard is shown in Reference 2. For the November 7, 1986 promulgation, the data from plant A were reviewed to determine whether the steam stripper was well-operated. The

Agency determined that 28 of the 40 data points were collected while the stripper was not well-operated; therefore, the Agency did not use these 28 data points for the calculation of the treatment standard.

Since the November 7, 1986 promulgation, the Agency collected steam stripping treatment performance data on F002 wastewaters from plant B. Analysis of the F002 wastewaters from plant B show that, relative to the characteristics of a waste that affect the performance of steam stripping, the F002 wastewaters from plant B are more difficult to treat than the F001-F005 wastewaters from plant A. A review of the data shows that the steam stripper at plant B achieved better treatment performance than the steam stripper at plant A. Therefore, the Agency is using these new data to promulgate a revised treatment standard of 0.44 ppm for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry.

2.0 AMENDMENT TO SECTION 3.2.4 OF THE BDAT BACKGROUND DOCUMENT FOR F001-F005 SPENT SOLVENTS

This section amends the discussion in Section 3.2.4 of the BDAT Background Document for F001-F005 Spent Solvents. This section presents characterization data for the spent solvent wastewaters from plant A and plant B.

Table 2-1 presents the ranges of constituents identified in F001-F005 wastewaters from plant A, which is a pharmaceuticals manufacturing facility. Table 2-2 presents the ranges of constituents identified in F002 wastewaters from plant B, which is an agricultural chemicals manufacturing facility. Analysis of the F002 wastewaters from plant B show that, relative to the characteristics of a waste that affect the performance of steam stripping, the F002 wastewaters from plant B are more difficult to treat than the F001-F005 wastewaters from plant A. Accordingly, EPA is transferring the level of treatment performance for F002 wastewaters from plant B to F001-F005 wastewaters from plant A. This determination is based on available characterization data and is further discussed in Section 4.1.2.

The data presented in Tables 2-1 and 2-2 were obtained from sampling and analysis episodes conducted by the Agency.

Table 2-1

AVAILABLE CHARACTERIZATION DATA FOR F001-F005 WASTEWATERS AT PLANT A

Constituent	Source of Data:	Concentration in the Untreated Waste (ppm) i	ii	iii
Methylene Chloride		225-12,000	8,879-11,837	NA
Methanol		NA	369-1,684	NA
Diethyl Ether		NA	32-45	NA
Pyridine		NA	289-600	NA
Total Dissolved Solids		NA	NA	2,000-4,000

(i) Plant A Data from the Development Document For Final Effluent Limitation Guidelines, New Source Performance Standards and Treatment Standards For the Pharmaceuticals Manufacturing Point Source Category (Reference 3).

(ii) Correspondence from Plant A to EPA, September 20, 1983 (Reference 4).

(iii) Comments from the Pharmaceutical Manufacturers Association to EPA, June 29, 1988 (Reference 6).

NA Not available.

Table 2-2

AVAILABLE CHARACTERIZATION DATA FOR F002 WASTEWATERS AT PLANT B

Constituent	Concentration in the Untreated Waste (ppm)
Carbon Tetrachloride	<2.5-3.1
Chloroform	23-110
Methylene Chloride	2,500-7,400
Hexachloroethane	0.26-1.3
Benzoic Acid	0.52
Methanol	55-81
Percent Water	91.97-97.11 (wt. %)

Parameter	Concentration in the Untreated Waste (ppm)
Total Dissolved Solids	88,900-122,300
Volatile Dissolved Solids	300-3,100

Data Source: Onsite Engineering Report for Plant B (Reference 5).

3.0 AMENDMENT TO SECTION 4.3 OF THE BDAT BACKGROUND DOCUMENT FOR F001-F005 SPENT SOLVENTS

This section amends Section 4.3 of the BDAT Background Document for F001-F005 Spent Solvents.

3.1 Applicable Treatment Technologies

For the November 7, 1986 promulgation, the Agency identified batch distillation, thin film evaporation, fractionation, incineration, steam stripping, biological treatment, carbon adsorption, air stripping, wet air oxidation, and fuel substitution as applicable treatment technologies for F001-F005. The Agency is not revising this list for the final rule.

3.2 Demonstrated Treatment Technologies

The demonstrated technology that the Agency has identified for treatment of methylene chloride in F001-F005 wastewaters from the pharmaceutical manufacturing industry is steam stripping (Reference 2). A detailed description of steam stripping is presented in Section 3.4.

3.3 Available Treatment Technologies

An available treatment technology is one that (1) can be purchased or licensed from the proprietor (i.e. commercially available), and (2)

substantially diminishes the toxicity of the waste or substantially reduces the likelihood of migration of hazardous constituents in the waste. For treatment of methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry, the demonstrated technology (steam stripping) meets these criteria and is therefore considered to be available.

3.4 Detailed Description of Steam Stripping

This section replaces the discussion of steam stripping in Section 4.3.1 of the BDAT Background Document for F001-F005 Spent Solvents.

Steam stripping is a distillation process which provides for the separation of constituents based on differences in volatility. More volatile constituents are separated from less volatile constituents by vaporization (addition of heat via steam) and condensation.

Applicability and Use of Technology. Steam stripping is applicable to wastewaters that contain BDAT organics that are sufficiently volatile such that they can be removed by the application of steam. Waste parameters that affect the applicability of steam stripping are filterable solids, total organic carbon (TOC), and the presence of BDAT organics that are either not volatile or only minimally volatile.

Underlying Principles of Operation. The basic principle of operation for steam stripping is the volatilization of hazardous constituents

through the application of heat. The constituents that are volatilized are then condensed and either reused or further treated.

An integral part of the theory of steam stripping is the principle of vapor-liquid equilibrium. When a liquid mixture of two or more components is heated, a vapor phase is created above the liquid phase. The vapor phase will be more concentrated in the constituents having the higher vapor pressure. If the vapor phase above the liquid phase is cooled to yield a condensate, a partial separation of the components results. The degree of separation would depend on the relative differences in the vapor pressures of the constituents; the larger the difference in the vapor pressure, the easier the separation can be accomplished.

If the difference between the vapor pressures is extremely large, a single separation cycle or single equilibrium stage of vaporization and condensation may achieve a significant separation of the constituents. If the difference between the vapor pressures is small, then multiple equilibrium stages are needed to achieve effective separation. In practice, the multiple equilibrium stages are obtained by stacking trays or placing packing into a column. The vapor phase from a tray rises to the tray above it and the liquid phase falls to the tray below it. Essentially, each tray represents one equilibrium stage. In a packed steam stripping column, the individual equilibrium stages are not discernible, but the number of equivalent trays can be calculated from mathematical relationships.

The vapor liquid equilibrium is expressed as relative volatility or the ratio of the vapor to liquid concentration for one constituent divided by the ratio of the vapor to liquid concentration of the other constituent. The relative volatility is a direct measure of the ease of separation. If the numerical value is 1, then separation is impossible because the constituents have the same concentrations in the vapor and liquid phases. Separation becomes easier as the value of the relative volatility becomes increasingly greater than unity.

Physical Description of the Process. A steam stripping unit consists of a boiler, a stripping section, a condenser, and a collection tank as shown by Figure 3-1. The boiler provides the heat required to vaporize the liquid fraction of the waste. The stripping section is composed of a set of trays or packing in a vertical column. The feed (waste influent) enters at the top.

The stripping process uses multiple equilibrium stages, with the initial waste mixture entering the uppermost equilibrium stage. The boiler is located below the lowermost equilibrium stage so that vapor generated moves upward in the column coming into contact with the falling liquid. As the vapor comes into contact with the liquid at each stage, the more volatile components are removed or "stripped" from the liquid by the vapor phase. The concentration of the emerging vapor is slightly enriched (as it is in equilibrium with the incoming liquid), and the liquid exiting the bottom of the boiler ("bottoms") is considerably enriched in the lower vapor pressure

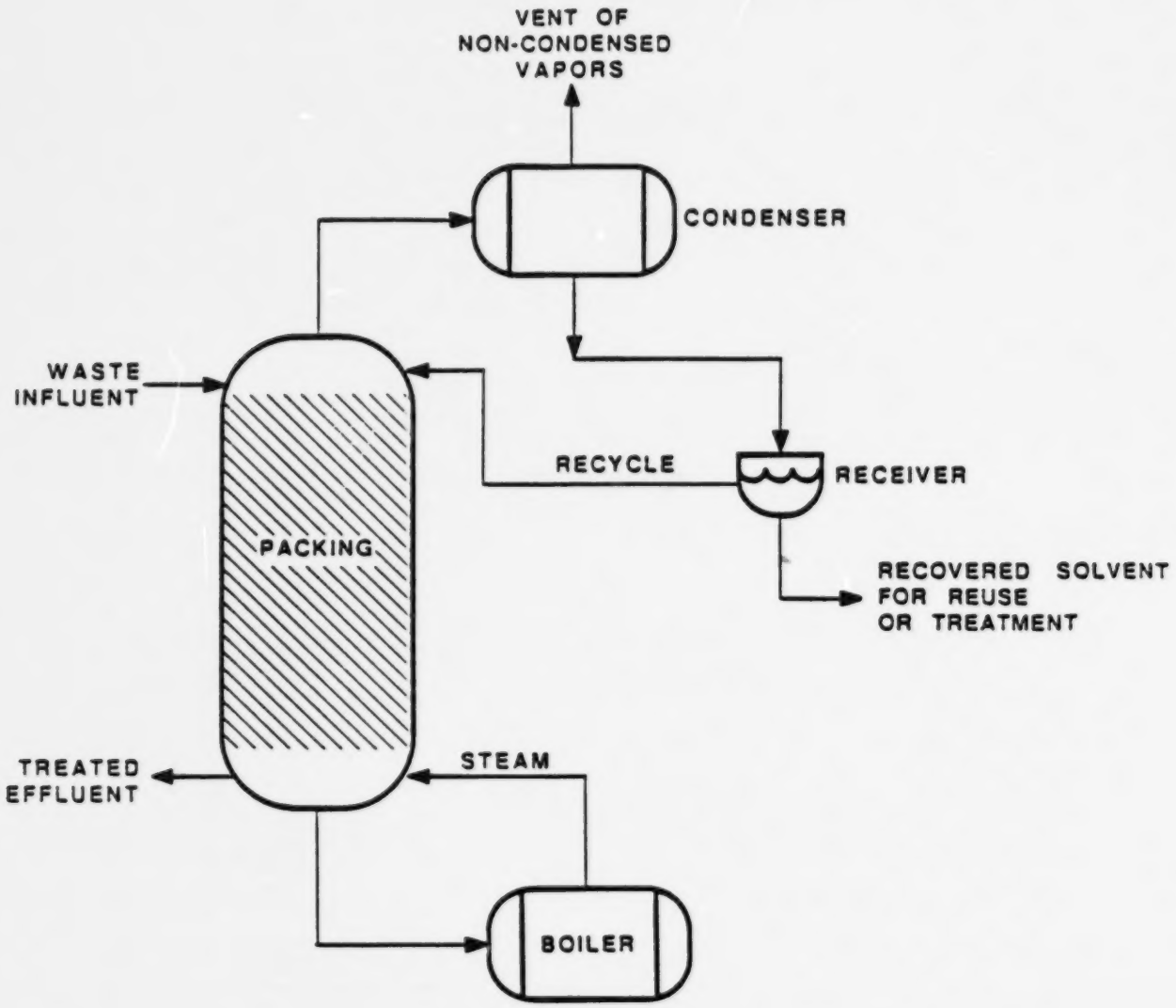

FIGURE 3-1.
STEAM STRIPPING

constituent(s). The process of stripping is very effective for wastewaters where the relative volatilities are large between the organics of concern and wastewater. Steam stripping is used to strip the organic volatiles from wastewater. The water effluent from the bottom of the stripper is reduced in organic content, but in some circumstances may require additional treatment, such as carbon adsorption or biological treatment. The steam and organic vapors leaving the top of the column are condensed. Organics in the condensate that form a separate phase in water usually can be separated and recovered or disposed. After separation the aqueous condensate is usually recycled to the stripper.

Characteristics of a Waste that Affect Performance. In determining whether steam stripping is likely to achieve the same level of performance on an untested waste as a previously tested waste, EPA focuses on the following characteristics of a waste: boiling point, total dissolved solids, total dissolved volatile solids, and oil and grease. EPA recognizes these characteristics have some limitations in assessing transfer of performance; nevertheless, the Agency believes that they provide the best possible indicator of relative volatility. Below is a discussion of relative volatility, as well as EPA's rationale for evaluating the above described waste characteristics in determining transfer of treatment performance.

As discussed earlier, the term relative volatility (α) refers to the ease with which a substance present in a solid or liquid waste will vaporize

from that waste upon application of heat from an external source. Hence, it bears a relationship to the equilibrium vapor pressure of the substance.

For an ideal* binary mixture, the relative volatility (α) is expressed as:

$$\alpha = \left\{\frac{K_i}{K_j}\right\} = \left\{\frac{Y_i/X_i}{Y_j/X_j}\right\}$$

where K_i and K_j are equilibrium concentrations for components i and j respectively, Y is the mole fraction of the component in the vapor, and X is the mole fraction of the component in the liquid.

For non-ideal binary mixtures, the relative volatility (α) is expressed as:

$$\alpha = \left\{\frac{Y_i}{X_i} \cdot \frac{f_{i,l}}{f_{i,v}}\right\} \Big/ \left\{\frac{Y_j}{X_j} \cdot \frac{f_{j,l}}{f_{j,v}}\right\}$$

where f is the fugacity. The term "fugacity" is a thermodynamic term that accounts for departures from ideal behavior of the gas and liquid; it can only be determined empirically.

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*The term "ideal" refers to whether the vapor pressures of the two components can be linearly related to their respective compositions in the liquid phase; this is known as Raoult's law. In general, binary solutions at low pressures follow this law and are, therefore, "ideal"; most mixtures do not follow Raoult's law.

EPA recognizes that the relative volatilities can not be measured or calculated directly for the types of wastes generally treated by steam stripping even if these wastes behaved in an ideal manner. Determining relative volatilities is further complicated by the fact that the relative volatility changes as the temperature conditions change throughout the steam stripper. Accordingly, EPA will use the following surrogates: boiling point, oil and grease content, total dissolved inorganic solids, and total dissolved volatile solids.

For a given pressure and temperature, compounds with lower boiling points will have higher vapor pressures. Therefore, in the case of wastewaters containing low concentrations of organics where relative volatility is effectively a comparison of vapor pressures, the ratio of boiling points of the constituents in the untested and tested wastes will indicate whether the untested waste can be treated to the same degree as the tested waste. Boiling point alone would not account for any non-ideal behavior of the solution. Accordingly, EPA will examine the concentrations of oil and grease, total dissolved solids, and total dissolved volatile solids. All of these characteristics affect the partial pressures of the individual organic constituents of concern as well as the solubility. Accordingly, these characteristics will affect relative volatility of a constituent and, hence, the ability of the constituent to be treated using steam stripping.

Design and Operating Parameters. EPA's analysis of whether a steam stripping system is well-designed will focus on the degree of separation the

system is designed to achieve and the controls installed to maintain the proper operating conditions. The specific parameters are presented below.

(1) Concentrations of Constituents in the Treated and Untreated Wastes. In determining whether to sample a particular steam stripper as a candidate for BDAT, EPA considers the concentration to which the system is designed to treat the waste. This evaluation is important for two reasons: a treatment system will usually not perform as well as designed; and if an untreated waste has concentrations of constituents in excess of the concentrations that the treatment system is designed to treat, the system performance will be poor. Therefore, in evaluating the performance of a steam stripper, data on the characteristics of the untreated waste are necessary to determine whether treatment performance conformed with design specifications.

(2) Vapor-Liquid Equilibrium Data. The vapor-liquid equilibrium data are determined in laboratory tests unless already available. The use of these data are required for several reasons. First, they are used to calculate the number of theoretical stages required to achieve the desired separation. Using the theoretical number of stages, the actual number of stages can then be determined through the use of empirical tray efficiency data supplied by an equipment manufacturer.

Second, the vapor-liquid equilibrium data are used to determine the liquid and vapor flow rates that ensure sufficient contact between the liquid

and vapor streams. These rates are, in turn, used to determine the column diameter.

(3) Column Temperature and Pressure. Column temperature and pressure are integrally related to the vapor liquid equilibrium conditions. Column temperature design includes performing a heat balance around the steam stripping unit, which accounts for the heat removed in the condenser, the heat input in the feed, the heat input from steam injectors, and the heat loss from the column. Column pressure influences the boiling point of the liquid. For example, the column temperature required to achieve the desired separation can be reduced by operating the system under vacuum. During treatment, it is important to continuously monitor these parameters to ensure that the system is operated at design conditions.

(4) Column Internals. Column internals are designed to accommodate the physical and chemical properties of the wastewater to be stripped. Two types of internals may be used in steam stripping: trays or packing. Tray types include bubble cap, sieve, valve and turbo-grid. Trays have several advantages over packing. Trays are less susceptible to blockage by solids, they have a lower capital cost for large diameter columns (greater than or equal to 3 feet), and they accommodate a wider range of liquid and vapor flow rates. Packing types include raschig rings, pall rings, saddles, and sulzer-structures. Compared to trays, packing has the advantages of having a lower pressure drop per theoretical stage, being more resistant to corrosive materials, having a lower capital cost for small diameter column (less than 3 feet),

and finally being less susceptible to foaming because of a more uniform flow distribution.

4.0 AMENDMENT TO SECTION 5.5.16 OF THE BDAT BACKGROUND DOCUMENT FOR F001-F005 SPENT SOLVENTS

This section amends Section 5.5.16 of the BDAT Background Document for F001-F005 Spent Solvents.

4.1 Identification of Best Demonstrated and Available Technology

For the November 7, 1986 promulgation, EPA determined steam stripping to be BDAT for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry. The treatment standard for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry is being revised in the final rule. This revision is based on new data for steam stripping of F002 wastewaters that have been determined to be more difficult to treat than F001-F005 wastewaters from the pharmaceuticals manufacturing industry. These data represent a level of performance that can be achieved by steam stripping of F001-F005 wastewaters from the pharmaceuticals manufacturing industry.

The Agency has 40 data points from plant A (Reference 3) for treatment of methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry. Table 4-1 presents the methylene chloride concentrations detected in the untreated and treated wastewaters at Plant A. These data are from a sampling episode conducted by the EPA's Industrial Technology Division. The Agency also has 13 data points from plant B (Reference 5) for

treatment of F002 wastewaters that have been determined to be more difficult to treat than F001-F005 wastewaters from the pharmaceuticals manufacturing industry. Table 4-2 presents the methylene chloride concentrations detected in the untreated and treated wastewaters at plant B. These data are from a sampling episode conducted by EPA's Office of Solid Waste. The data from plant A were used for the November 7, 1986 promulgation; the data from plant B were obtained by EPA after the November 7, 1986 promulgation date.

The treatment performance data were assessed to determine whether they represent operation of a well-designed and well-operated system, whether quality assurance/quality control measures were employed to ensure the accuracy of the data, and whether appropriate analytical tests were used to assess the performance of the treatment technology. Section 4.1.1 presents the analysis of operation of plant A, and Section 4.1.3 presents the analysis of operation of plant B. Section 4.1.2 presents the Agency's determination that the F002 wastewaters from plant B are more difficult to treat than F001-F005 wastewaters from the pharmaceuticals manufacturing industry, and that the treatment performance data for F002 wastewaters from plant B represent a level of performance that can be achieved by steam stripping of F001-F005 wastewaters from the pharmaceuticals manufacturing industry.

4.1.1 Analysis of Operation of Plant A

The performance data for steam stripping of F001-F005 wastewaters containing methylene chloride at plant A were reviewed to determine whether

the steam stripper was well-designed and well-operated during the sampling episode. Design and operating data collected at plant A during the sampling episode are presented in Table 4-3. Design conditions are available for overhead temperature; therefore, only overhead temperature data are presented. Operating data, including feed temperature, bottoms temperature, feed rate, and steam rate, can be found in Reference 3.

As discussed in Section 3.0 of this amendment, temperature is an important operating parameter. The steam stripping column must be designed to achieve the proper operating conditions to obtain optimal treatment performance. The steam stripper at plant A is designed to effectively treat the waste at an overhead temperature of 98°C. As shown in Table 4-3, many data points were collected during operation at overhead temperatures below 98°C. During the sampling episode, the overhead temperature ranged from 82°C to 98°C, with only one data point collected while the stripper was operated at the design temperature of 98°C. This wide fluctuation of overhead temperature indicates poor operation of the steam stripper.

In the development of treatment standards, the Agency eliminates all data from poorly designed or operated treatment systems. For plant A, the Agency has limited design data. For the November 7, 1986 promulgation, using these limited design data, the Agency attempted to determine which data from plant A were collected when the treatment system represented a well-designed and well-operated system. The treatment performance data from plant A were examined to determine the minimum temperature representative of a well-

operated system. As a method of evaluating the data, the concentration of methylene chloride in the effluent was plotted as a function of overhead temperature. The data indicate that, as the overhead temperature drops below the design temperature, there is an increase in the variability in the effluent concentrations achieved at a given overhead temperature. This increased variability is an indication of increased instability or poor control of the steam stripping system. Since the variability in the effluent concentrations increased as the overhead temperature dropped below 90°C, the minimum overhead temperature for a system that was well-operated was estimated as 90°C. As a result of this evaluation, for the November 7, 1986 rule, 28 of the 40 data points were deleted from the data set because the overhead temperature was below 90°C. Based on the limited design data available, the Agency performed the preceding analyses to determine which data points represented a well-designed and well-operated system.

Since the November 7, 1986 promulgation, the Agency has collected treatment performance data from plant B. The Agency has designed data for plant B to more accurately determine if plant B was well-designed and well-operated during sample collection. Because the Agency has these design data (see Section 4.1.3) and has determined that the wastewaters from plant B are more difficult to treat than the wastewaters from plant A (see Section 4.1.2), the Agency is using the treatment performance data from plant B in setting treatment standards for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry.

4.1.2 Determination that Plant B F002 Wastewaters are More Difficult to Treat than Plant A F001-F005 Wastewaters

Since November 7, 1986, data from plant B for steam stripping treatment of methylene chloride in F002 wastewaters have become available to the Agency. The data for the untreated F002 wastewaters from plant B were compared to the data for the untreated F001-F005 pharmaceuticals manufacturing industry wastewaters from plant A. To compare the data for these wastewaters, the Agency considered the characteristics of a waste that affect the performance of a steam stripper, as well as other characteristics of the waste that provide information on the treatability of the waste by steam stripping.

Methylene chloride concentration data are available to the Agency for the untreated wastewaters at plant A and at plant B. The methylene chloride concentration in the untreated F001-F005 wastewaters at plant A ranged from 225 ppm to 12,000 ppm, while the methylene chloride concentration in the untreated F002 wastewaters at plant B ranged from 2,500 ppm to 7,400 ppm. The Agency also has data for methanol concentrations in the untreated wastewaters at plant A and at plant B. Methanol concentrations in the untreated F001-F005 wastewaters from plant A ranged from 369 to 1,684 ppm, while the methanol concentrations in the untreated F002 wastewaters from plant B ranged from 55 to 81 ppm. The Agency recognizes that there is a difference in methanol concentrations; however, the Agency believes that the concentration of methanol would not affect the performance of the treatment

system because methanol has a higher boiling point than methylene chloride and methanol does not form an azeotrope with methylene chloride.

In Section 3.4, the Agency identified the following waste characteristics that affect performance of steam stripping: boiling point, oil and grease, total dissolved inorganic solids, and total dissolved volatile solids. Methylene chloride is the only constituent in either waste for which the treatment standard is being revised at this time; the boiling point of pure methylene chloride is 39.75°C. EPA has data from plant B on total dissolved solids and total dissolved volatile solids, but does not have data from plant B on oil and grease. EPA has data from plant A on total dissolved solids, but does not have data from plant A on the other characteristics. The concentration of dissolved solids in the untreated F001-F005 pharmaceuticals manufacturing industry wastewaters from plant A ranged from 2,000 to 4,000 ppm, while the concentration of dissolved solids in the untreated F002 wastewaters from plant B ranged from 89,000 to 122,000 ppm. The Agency believes that the F002 wastewaters from plant B with higher concentrations of total dissolved solids are more difficult to treat than the F001-F005 wastewaters from plant A.

Based on the above considerations, the Agency has determined that the untreated F002 wastewaters from plant B are more difficult to treat than the untreated F001-F005 wastewaters from plant A, and that the treatment performance data for F002 wastewaters from plant B represent a level of per-

formance that can be achieved by steam stripping of F001-F005 wastewaters from the pharmaceuticals manufacturing industry. EPA has thus considered data from plant B in revising the treatment standard for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry.

4.1.3 Analysis of Operation of Plant B

The performance data for steam stripping of F002 wastewaters containing methylene chloride at plant B were reviewed to determine whether the steam stripper could be considered well-designed and operated. Design and operating data for plant B are presented in Table 4-4. Design conditions are available for mid-column temperature; therefore, only mid-column temperature data are presented. Other operating data, including feed flowrate and column overhead temperature, can be found in Reference 5.

The Agency also has equilibrium data used in the design of the steam stripper at plant B. These data are presented in Reference 5. An analysis of these data, along with an analysis of the operating data, indicate that the stripper was well designed and well operated during the time of sample collection. The mid-column operating temperature ($95^{o}C$-$102^{o}C$) was well above the designed minimum mid-column temperature ($95^{o}C$) and showed little fluctuation during sampling. Other operating conditions as found in Reference 5 showed little fluctuation, indicating a well-operated system.

The Agency now has data from plant B for which EPA can accurately determine if the treatment system was well-designed and well-operated during

sampling. The Agency did not have these data available for plant A for the November 7, 1986 promulgation. Therefore, the Agency could not determine as accurately for plant A as for plant B if the facility was well-designed and well-operated during sampling. Because the Agency has these new data, and because the data indicate a well-designed and well-operated system that achieves better treatment performance on a wastewater which is more difficult to treat than the wastewater from plant A, EPA is not including the data from plant A in the revision of the treatment standard for methylene chloride. Instead, EPA is using only the treatment data from plant B to calculate the revised treatment standard.

4.2 Calculation of Treatment Standards

The best demonstrated and available technology for treatment of methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry has been identified as steam stripping based on available performance data. The best measure of performance of a destruction, recovery, or separation technology, such as steam stripping, is the total amount of constituent remaining after treatment. Therefore, the BDAT treatment standard for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry was calculated based on total waste concentration data.

The Agency used the data from plant B, consisting of 13 data points, to calculate the revised treatment standard for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry. Table 4-2 presents the 13 values of the concentration of methylene chloride in the

treated waste. EPA adjusted these data to account for analytical interferences associated with the chemical makeup of the treated wastes. Generally, performance data are corrected for accuracy as follows: (1) a matrix spike recovery is determined for the constituent as explained below, (2) an accuracy correction factor is determined for the constituent by dividing 100 by the matrix spike recovery (percent); and (3) treatment performance data for the constituent are corrected by multiplying the reported concentration of the constituent by the corresponding accuracy correction factor.

Matrix spike recoveries are developed by analyzing a sample of a treated waste for a constituent and then reanalyzing the sample after the addition of a known amount of the same constituent (i.e., spike) to the sample. The matrix spike recovery represents the total amount of constituent recovered after spiking minus the initial concentration of the constituent in the sample, and the result divided by the known amount of constituent added.

Table 4-5 presents the matrix spike recoveries for volatile organic constituents for which matrix spike analyses were performed at plant B. A matrix spike analysis was not performed for methylene chloride. Matrix spike analyses were performed on Sample 1 and Sample 7 for other volatile organic constituents. Therefore, the recoveries determined for the volatile organic constituents for which matrix recoveries were performed were averaged separately for the two matrix spike analyses. The average matrix spike recovery for volatiles in Sample 1 was 102%; the average recovery for volatiles in

Sample 7 was 110%. The lower average percent recovery, 102%, was used in accuracy correction calculations for methylene chloride.

Methylene chloride was not detected in 11 of the 13 treated wastewater samples. In these cases, the detection limits were presented as the corrected treatment concentrations for methylene chloride. For the two cases where methylene chloride was detected in the samples, the treatment concentrations were adjusted by multiplying the treatment concentrations by the accuracy correction factor (0.98).

The corrected treatment concentrations for methylene chloride in F002 wastewaters treated by steam stripping at plant B are presented in Table 4-6.

The revised treatment standard for methylene chloride in F001-F005 wastewater from the pharmaceuticals manufacturing industry has been calculated as shown in Table 4-7. The steps used to calculate the revised treatment standard are as follows. The arithmetic average of the corrected treatment data for methylene chloride was calculated for the data set using the data points presented in Table 4-6. Using the corrected treatment data, a variability factor was calculated for the data set. The variability factor represents the variability inherent in performance of treatment systems, collection of treated samples, and analyses of samples. For cases where methylene chloride was not detected in the treated wastewater, the Agency used the detection limit in calculation of the variability factor. Variability is

still expected in concentrations below the detection limit since the actual concentrations would range from zero to the detection limit. Methylene chloride was present at concentrations greater than the detection limit in two samples (samples 8 and 11); methylene chloride was not detected in the other eleven samples. Therefore, the variability factor was calculated based on eleven data points set at the detection limits and two data points representing methylene chloride concentrations that were detected in the samples.

The revised treatment standard for methylene chloride was calculated by multiplying the average corrected treatment concentration of methylene chloride in the treated waste by the variability factor. As shown in Table 4-7, the revised treatment standard for methylene chloride in F001-F005 wastewaters from the pharmaceuticals manufacturing industry is 0.44 ppm.

Table 4-1

TREATMENT PERFORMANCE DATA COLLECTED BY EPA
FOR F001-F005 WASTEWATERS CONTAINING METHYLENE CHLORIDE
PLANT A - STEAM STRIPPING

Sample Number	Untreated Wastewater Methylene Chloride Concentration (ppm)	Treated Wastewater Methylene Chloride Concentration (ppm)
1	8,250	0.926
2	8,250	5.10
3	8,250	4.94
4	8,250	3.00 *
5	8,250	1.99 *
6	8,250	5.70 *
7	8,250	22.80 *
8	8,250	38.05 *
9	225	3.90 *
10	225	8.36 *
11	225	20.60 *
12	225	4.07
13	225	10.70 *
14	225	20.30 *
15	225	4.80 *
16	225	7.87 *
17	7,000	1.72
18	7,000	1.63
19	7,000	3.60 *
20	7,000	14.25 *
21	7,000	39.30 *
22	7,000	138.0 *
23	7,000	110.0 *
24	7,000	60.80 *
25	11,200	10.10 *
26	9,900	22.85 *
27	9,100	57.50 *
28	9,400	115.0 *
29	10,200	59.90 *
30	11,800	127.0 *
31	10,000	3.18
32	12,000	3.73 *

Table 4-1 (Continued)

TREATMENT PERFORMANCE DATA COLLECTED BY EPA
FOR F001-F005 WASTEWATERS CONTAINING METHYLENE CHLORIDE
PLANT A - STEAM STRIPPING

Sample Number	Untreated Wastewater Methylene Chloride Concentration (ppm)	Treated Wastewater Methylene Chloride Concentration (ppm)
33	9,500	7.20
34	9,500	4.04
35	9,500	4.27
36	9,500	1.47
37	9,500	1.62 *
38	9,500	2.63
39	9,500	7.83 *
40	9,500	15.80 *

Reference 3

*This data point was deleted in data analysis for the November 7, 1986 promulgation because the overhead temperature was less than 90°C. See Section 4.1.1 of this document for a discussion of this data editing procedure.

Table 4-2

TREATMENT PERFORMANCE DATA COLLECTED BY EPA
FOR F002 WASTEWATERS CONTAINING METHYLENE CHLORIDE
PLANT B - STEAM STRIPPING

Sample Number	Untreated Wastewater Methylene Chloride Concentration (ppm)	Treated Wastewater Methylene Chloride Concentration (ppm)
1	3,400	<0.250
2	2,900	<0.250
3	2,500	<0.170
4	3,000	<0.170
5	5,400	<0.250
6	7,400	<0.250
7	3,900	<0.110
8	3,200	0.120
9	3,100	<0.125
10	3,600	<0.170
11	2,800	0.400
12	3,400	<0.170
13	5,500	<0.125

Reference 5.

Table 4-3

DESIGN AND OPERATING DATA COLLECTED BY EPA
PLANT A - STEAM STRIPPING

Sample Number	Overhead Temp(°C) (Design=98°C)	Sample Number	Overhead Temp(°C) (Design=98°C)
1	97	21	84*
2	98	22	83*
3	94	23	83*
4	89*	24	83*
5	89*	25	89*
6	86*	26	86*
7	84*	27	84*
8	84*	28	83*
9	87*	29	83*
10	89*	30	82*
11	86*	31	93
12	90	32	89*
13	89*	33	90
14	86*	34	90
15	87*	35	95
16	85*	36	90
17	97	37	89*
18	90	38	90
19	88*	39	88*
20	85*	40	88*

Reference 3.

*This data point was deleted in data analysis for the November 7, 1986 promulgation because the overhead temperature was less than 90°C. See Section 4.1.1 of this document for a discussion of this data editing procedure.

Table 4-4

DESIGN AND OPERATING DATA COLLECTED BY EPA
PLANT B - STEAM STRIPPING

Sample Number	Mid-Column Temp(°C) (Min.80°C)
1	102
2	102
3	101
4	100
5	99
6	100
7	100
8	100
9	99
10	101
11	100
12	100
13	101

Reference 5.

Table 4-5

VOLATILE MATRIX SPIKE RECOVERIES FOR STEAM STRIPPER BOTTOMS FROM PLANT B

Spike Constituent	Sample Set 1 Original Amount Found (ppm)	Sample Set 1 Amount Spiked (ppm)	Sample Set 1 Amount Recovered (ppm)	Sample Set 1 Percent* Recovery (%)	Sample Set 7 Original Amount Found (ppm)	Sample Set 7 Amount Spiked (ppm)	Sample Set 7 Amount Recovered (ppm)	Sample Set 7 Percent* Recovery (%)
4. Benzene	<0.25	2.5	2.625	105	<0.11	1.085	1.118	103
9. Chlorobenzene	<0.25	2.5	2.4	96	<0.11	1.085	1.237	114
38. Methylene Chloride	No matrix spike was performed for this constituent. The percent recovery for methylene chloride is based on the lower average percent recovery of the volatile constituents. The lower average percent recovery is 102% from Sample Set 1.							
43. Toluene	<0.25	2.5	2.475	99	<0.11	1.085	1.15	106
45. 1,1,1-Trichloroethane	<0.25	2.5	2.6	104	<0.11	1.085	1.302	120
47. Trichloroethene	<0.25	2.5	2.65	106	<0.11	1.085	1.139	105
			Average	102			Average	110

*Percent Recovery = 100 x $(C_i - C_o)/C_t$, where C_i = amount recovered, C_o = original amount found, and C_t = amount spiked.

Table 4-6

CORRECTED METHYLENE CHLORIDE CONCENTRATIONS
FOR STEAM STRIPPER BOTTOMS (F002 TREATED WASTEWATER)
FROM PLANT B

Sample Number	Corrected Concentration** in the Treated Wastewater, ppm Plant B
1	0.250
2	0.250
3	0.170
4	0.170
5	0.250
6	0.250
7	0.110
8*	0.118
9	0.125
10	0.170
11*	0.392
12	0.170
13	0.125
Average	0.196

*Methylene chloride was present at concentrations above the detection limit in samples 8 and 11; methylene chloride was not detected in the other samples.

**Corrected concentrations are equal to the actual concentration multiplied by the accuracy correction factor for samples where methylene chloride was found above the detection limit. Corrected concentrations are equal to the detection limit in samples where methylene chloride was not detected.

Table 4-7

CALCULATION OF THE TREATMENT STANDARD FOR METHYLENE CHLORIDE IN F001-F005 WASTEWATERS FROM THE PHARMACEUTICALS MANUFACTURING INDUSTRY

Data Set	Range in Untreated Waste (ppm)	Arithmetic Average of Corrected Treated Values (ppm)	Variability Factor (VF)	Treatment Standard (Average x VF) (ppm)
Plant B	2,500- 7,400	0.196	2.26	0.44

5.0 REFERENCES

1. Chemical Manufacturers Association. 1986. Comment on EPA's Proposed Rule on Land Disposal Restrictions, pp. III-25, 26, and 28. Volume IX, Commenter No. 85.

2. USEPA. 1986. U.S. Environmental Protection Agency, Office of Solid Waste. Best Demonstrated Available Technology (BDAT) Background Document For F001-F005 Spent Solvents. Vol 2, pp. 5-62 to 5-70, 5-159 to 5-162. November 1986.

3. USEPA. 1983. U.S. Environmental Protection Agency, Office of Water. Development Document for Final Effluent Guidelines, New Source Performance Standards and Pretreatment Standards for the Pharmaceutical Manufacturing Point Source Category. pp. 124-128. September 1983.

4. Correspondence from Hoffman-LaRoche, Inc., to EPA. September 3, 1983.

5. USEPA. 1988. U.S. Environmental Protection Agency, Office of Solid Waste. Onsite Engineering Report of Treatment Technology Performance and Operation for Olin Chemicals, Rochester, New York. pp. 8, 12, 35-46, 64. July 22, 1988.

6. Comments received by U.S. EPA from the Pharmaceutical Manufacturers Association, June 29, 1988.